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TITLE: Silicon source reagent compositions, and method of making
and using same for microelectronic device structure

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Abstract Text - ABTX (1):

A method of synthesizing an aminosilane source reagent composition, by reacting an aminosilane precursor compound with an amine source reagent compound in a solvent medium comprising at least one activating solvent component, to yield an aminosilane source reagent composition having less than 1000 ppm halogen.

Application Filing Date - AD (1):

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Brief Summary Text - BSTX (4):

The process of fabricating semiconductor integrated circuits generally includes the formation of such components as, gate oxides, high k dielectrics, low k dielectrics, barrier layers, etch stop layers and gate spacers. Such components often include silicon or silicon oxide in their compositions. For example, conventional gate dielectric materials may be formed from silicon dioxide, silicon oxy-nitride, silicon nitride or metal silicates.

Brief Summary Text - BSTX (7):

SiO.sub.2 represents the highest quality gate dielectric material 180 so far developed in silicon technology with low defects and low surface state density. One important advantage of SiO.sub.2 is that it may be grown from the silicon substrate at elevated temperatures in an oxidizing environment. It is well known in the art, that thermally grown oxides tend to have fewer defects, (i.e. pinholes), than deposited materials. Thus, SiO.sub.2 has persisted as the dielectric material in most silicon device structures.

Brief Summary Text - BSTX (9):

As devices have scaled to smaller and smaller dimensions, the gate dielectric thickness has continued to shrink. Although further scaling of devices is still possible, scaling of the gate dielectric thickness has almost

reached its practical limit with the conventional gate dielectric materials; silicon dioxide, silicon oxy-nitride and silicon nitride. Further scaling of silicon dioxide gate dielectric thickness will involve problems such as: extremely thin layers allowing for large leakage currents due to direct tunneling through the oxide. Because such layers are formed literally from a few atomic layers, exact process control is required to repeatably produce such layers. Uniformity of coverage is also critical because device parameters may change dramatically based on the presence or absence of even a single monolayer of dielectric material. Finally, such thin layers form poor diffusion barriers to impurities and dopants.

Brief Summary Text - BSTX (10):

Consequently, there is a need in the art for alternative dielectric materials, which can be formed in a thicker layer than silicon dioxide and yet still produce the same field effect performance. This performance is often expressed as "equivalent oxide thickness" (EOT). Although the alternative material layer may be thick, it has the equivalent effect of a much thinner layer of silicon dioxide (commonly called simply "oxide"). In order to have a physically thick layer with a low EOT, the dielectric constant of the insulating material must be increased. Many, if not most, of the attractive alternatives for achieving low equivalent oxide thicknesses are metal oxides, such as tantalum pentoxide, titanium dioxide, barium strontium titanate and other suitable thin films.

Brief Summary Text - BSTX (11):

However, the formation of such metal oxides as gate dielectrics has been found to be problematic. At typical metal oxide deposition temperatures, the oxygen co-reactant or oxygen-containing precursor tends to oxidize the silicon substrate, producing a lower dielectric constant oxide layer at the interface between the substrate and the higher dielectric constant, gate dielectric material. It could be that the transition metal oxide acts as a catalytic source of activated oxygen, that the precursor molecules increase the oxygen activity or that oxygen from the precursor is incorporated in the growing oxide film. Whatever the cause, the presence of this interfacial oxide layer increases the effective oxide thickness, reducing the effectiveness of the alternative gate dielectric material. The existence of the interfacial oxide layer places a severe constraint on the performance of an alternative dielectric field effect device and therefore, is unacceptable.

Brief Summary Text - BSTX (12):

The use of metal oxide and metal oxy-nitride thin films comprising Zr, Hf, Y, La, Lanthanide series elements, Ta, Ti and/or Al and silicates of these

metal oxides and metal oxy-nitrides are regarded as potential material replacements of the SiO₂ gate oxides, (i.e., U.S. Pat. Nos. 6,159,855 and 6,013,553). However, to ensure a high integrity interface between the silicon and the gate dielectric film these films must be deposited at relatively low temperatures.

Brief Summary Text - BSTX (13):

The source reagents and methodology employed to form such gate dielectric thin films are extremely critical for the provision of a gate structure having satisfactory electrical performance characteristics in the product device. Specifically, the source reagents and methodology must permit the gate dielectric thin film to form on a clean silicon surface, without the occurrence of side reactions producing predominantly silicon dioxide (SiO₂), locally doped SiO₂ and/or other impurities, that lower the dielectric constant and compromise the performance of the product microelectronic device. Accordingly, the absence of impurities is highly desirable.

Brief Summary Text - BSTX (14):

Chemical vapor deposition (CVD) is the thin film deposition method of choice for high-density, large-scale fabrication of microelectronic device structures, and the semiconductor manufacturing industry has extensive expertise in its use. Metalorganic CVD (MOCVD) and more particularly atomic layer CVD (ALCVD) are particularly advantageous processes because they allow for lower deposition temperatures and stricter control of the stoichiometry and thickness of the formed layer.

Brief Summary Text - BSTX (18):

Excess halide may adversely affect a gate dielectric thin film in either of two ways. Halide incorporation into a gate dielectric thin film, may directly affect the electronic nature of the film, thereby reducing device lifetime. Secondly, halide, such as chloride, leads to formation of hydrogen chloride during the decomposition of the precursor, which potentially affects the CVD chamber making the treatment of the effluent from the chamber more challenging.

Brief Summary Text - BSTX (20):

In such applications, the choice of the zirconium or hafnium CVD source reagents and a compatible silicon source reagent is of critical importance for the successful deposition of high quality Zr or Hf silicate gate dielectric. Low temperature CVD silicon precursors are required to minimize the formation of interfacial silicon dioxide. Ideally, the precursors are compatible in solution and in vapor phase and decompose below 600.degree. C. on substrate surfaces, forming Hf or Zr silicates in high purity and high density with no

interfacial layer.

Brief Summary Text - BSTX (24):

Silicon amide source reagents are of great interest for use as low temperature CVD precursors in many applications, e.g., CVD of silicon nitride and early transition metal silicates. However, many commercially available silicon amides have unacceptably high levels of chloride.

Brief Summary Text - BSTX (32):

The present invention relates to novel precursor compositions for low temperature (<600.degree. C.) chemical vapor deposition (CVD) formation of silicon-containing films, and to associated methods of making and using such types of compositions.

Brief Summary Text - BSTX (36):

In one broad aspect, the present invention relates to silicon precursors having reduced oxygen and halogen content (relative to various corresponding commercial silicon source reagents) with utility for chemical vapor deposition (CVD) of silicon containing thin films of varying types, including silicon nitride, silicates, and doped silicate films (when a dopant co-precursor is utilized), as well as to a method for making and using such silicon precursors. More specifically, the silicon precursors of the present invention comprise a composition selected from the group consisting of:

R³SiA_y(NR¹R²)_{4-x-y} and (2)

Brief Summary Text - BSTX (37):

##STR00001## wherein R³ is selected from the group consisting of hydrogen, C₁₋₄ alkyl, and C₁₋₄ alkoxy; x is from 0 to 3; Si is silicon; A is halogen; y is from 0 to 3; N is nitrogen; each of R¹ and R² is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁₋₈ alkyl, and C₁₋₈ perfluoroalkyl; and n is from 1 to 6.

Brief Summary Text - BSTX (38):

In a further aspect, the present invention relates to novel, stable aminosilane source reagent compositions for chemical vapor deposition (CVD) of silicon-containing thin films as well as to methods of making and using same. More specifically, the present invention relates to novel aminosilane source reagent compositions having the formula, R³SiA_y(NR¹R²)_{4-x-y}; (2) wherein R³ is selected from the group consisting of hydrogen, C₁₋₄ alkyl, and C₁₋₄ alkoxy; x is from 0 to 3; Si is silicon; A is halogen; y is

from 0 to 3; N is nitrogen; R.sup.1 is methyl and R.sup.2 ethyl.

Brief Summary Text - BSTX (41):

A still further aspect of the invention relates to a microelectronic device structure comprising a substrate having a chemical vapor deposited silicon-containing thin film layer on the substrate, wherein the silicon containing layer has been formed using a liquid-phase silicon precursor that is thermally stable at liquid delivery temperatures (at which the precursor liquid is vaporized to form a corresponding precursor vapor), but which is readily decomposable at chemical vapor deposition condition temperatures, to yield a silicon-containing film on the substrate with which the precursor vapor is contacted

Description Paragraph - DETX (3):

FIGS. 2A and 2B show a limited pressure-temperature matrix for Si(N(C.sub.2H.sub.5).sub.2).sub.2Cl.sub.2(bis(diethyl-amino)dichlorosilan- e), and Si(N(CH.sub.3).sub.2).sub.3Cl (tris(dimethyl-amino)chlorosilane in N.sub.2O.

Description Paragraph - DETX (16):

Aminosilane precursor compounds useful in the synthetic process of the instant invention must have reactive leaving groups, such as H and/or halogen. In one embodiment, aminosilane precursor compounds useful in the instant invention include but are not limited to, silicon halides, alkylsilanes and other aminosilanes. Preferably, the aminosilane precursor compound is a silicon halide compound comprising a composition selected from the group consisting of: R.sup.3.sub.xSiA.sub.y(NR.sup.1R.sup.2).sub.4-x-y and (4)

Description Paragraph - DETX (17):

##STR00002## wherein R.sup.3 is selected from the group consisting of hydrogen, C.sub.1 C.sub.4 alkyl, and C.sub.1 C.sub.4 alkoxy; x is from 0 to 3; Si is silicon; A is halogen; y is from 1 to 4; N is nitrogen; each of R.sup.1 and R.sup.2 is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C.sub.1 C.sub.8 alkyl, and C.sub.1 C.sub.8 perfluoroalkyl; and n is from 1 6. Preferably, A is Cl.

Description Paragraph - DETX (19):

##STR00003## wherein B is selected from the group consisting of H, Li, Na, K, Zn and MgBr; N is nitrogen; R.sup.1 and R.sup.2 are same or different and each is independently selected from the group consisting of H, aryl, perfluoroaryl, C.sub.1 C.sub.8 alkyl, and C.sub.1 C.sub.8 perfluoroalkyl; and n is from 1 6. Preferably, R.sup.1 and R.sup.2 are methyl and/or ethyl.

Description Paragraph - DETX (36):

The period of time required for reactions to complete and the temperature at which they are run, are parameters readily determined by those skilled in the art. Such determinations are based on parameters such as pressure, concentration, mixing speed etc.

Description Paragraph - DETX (37):

In one embodiment, the reaction mixture of step (1) as outlined hereinabove, wherein the aminosilane precursor compound is combined with the amine source reagent compound, should be carried out at a temperature that is in the range of from about -30.degree. C. to room temperature and a pressure that is about one atmospheric pressure. Preferably the combination of the compounds is carried out at a temperature of .+-.0.degree. C. and a pressure that is about one atm.

Description Paragraph - DETX (38):

In a further embodiment, the reaction mixture of step (3) as outlined hereinabove, wherein the aminosilane precursor compound having partially substituted leaving groups, is combined with the amine source reagent compound, and the polar activating solvent, should be carried out at a temperature that is in the range of from about 0.degree. C. to 100.degree. C. at ambient pressure. Preferably the reaction of step (3) is carried out a temperature that is .+-.60.degree. C. at an ambient pressure.

Description Paragraph - DETX (39):

The aminosilane source reagent compositions synthesized in the aforementioned procedures, are crude product and must be isolated and purified. Such isolation and purification methods are readily available and known to those skilled in the instant art. Preferably the crude aminosilane source reagent composition is separated from the by-product by filtration or decantation and preferably the separated aminosilane source reagent composition is further purified by distillation to produce an aminosilane source reagent composition having a halogen level of less than 1000 ppm, preferably less than 500 ppm and most preferably less than 10 ppm.

Description Paragraph - DETX (41):

In one embodiment, the present invention relates to silicon precursors made by reacting an aminosilane precursor compound with an amine source reagent compound in a solvent medium comprising at least one activating solvent component, to yield an aminosilane source reagent composition having a halogen content that is less than 1000 ppm, said aminosilane source reagent composition

selected from the group consisting of:

R.sup.3.sub.xSiA.sub.y(NR.sup.1R.sup.2).sub.4-x-y and (2)

Description Paragraph - DETX (42):

##STR00004## wherein R.sup.3 is selected from the group consisting of hydrogen, C.sub.1 C.sub.4 alkyl, and C.sub.1 C.sub.4 alkoxy; x is from 0 to 3; Si is silicon; A is halogen; Y is from 0 to 3; N is nitrogen; each of R.sup.1 and R.sup.2 is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C.sub.1 C.sub.8 alkyl, and C.sub.1 C.sub.8 perfluoroalkyl; and n is from 1 6.

Description Paragraph - DETX (43):

In a further embodiment, the present invention relates to novel, stable aminosilane source reagent compositions having formula:

R.sup.3.sub.xSiA.sub.y(NR.sup.1R.sup.2).sub.4-x-y (2) wherein R.sup.3 is selected from the group consisting of hydrogen, C.sub.1 C.sub.4 alkyl, and C.sub.1 C.sub.4 alkoxy; x is from 0 to 3, A is Cl, y is from 0 to 3; R.sup.1 is methyl; and R.sup.2 is ethyl.

Description Paragraph - DETX (49):

##STR00005## wherein R.sup.3 is selected from the group consisting of hydrogen, C.sub.1 C.sub.4 alkyl, and C.sub.1 C.sub.4 alkoxy; x is from 0 to 3; Si is silicon; A is halogen; Y is from 0 to 3; N is nitrogen; each of R.sup.1 and R.sup.2 is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C.sub.1 C.sub.8 alkyl, and C.sub.1 C.sub.8 perfluoroalkyl; and n is from 1 6; and the dopant precursor is a metalloamide source reagent composition selected from the group consisting of: M(NR.sup.1R.sup.2).sub.x; and (9)

Description Paragraph - DETX (50):

##STR00006## wherein, M is selected from the group consisting of: Zr, Hf, Y, La, Lanthanide series elements, Ta, Ti, Al; N is nitrogen; each of R.sup.1 and R.sup.2 is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C.sub.1 C.sub.8 alkyl, C.sub.1 C.sub.8 perfluoroalkyl, alkylsilyl; x is the oxidation state on metal M; and n is from 1 6.

Description Paragraph - DETX (54):

In a further embodiment, the present invention relates to a CVD precursor composition for forming a silicon containing thin film on a substrate, said precursor composition made by reacting an aminosilane precursor compound with an amine source reagent compound in a solvent medium comprising at least one

activating solvent component, to yield an aminosilane source reagent composition having a halogen content that is less than 1000 ppm, said precursor composition including at least one aminosilane source reagent composition selected from the group consisting of:

R.sup.3.sub.xSiA.sub.y(NR.sup.1R.sup.2).sub.4-x-y and (2)

Description Paragraph - DETX (55):

##STR00007## wherein R.sup.3 is selected from the group consisting of hydrogen, C.sub.1 C.sub.4 alkyl, and C.sub.1 C.sub.4 alkoxy; x is from 0 to 3; Si is silicon; A is halogen; Y is from 0 to 3; N is nitrogen; each of R.sup.1 and R.sup.2 is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C.sub.1 C.sub.8 alkyl, and C.sub.1 C.sub.8 perfluoroalkyl; and n is from 1 to 6.

Description Paragraph - DETX (58):

##STR00008## wherein M is selected from the group consisting of: Zr, Hf, Y, La, Lanthanide series elements, Ta, Ti, Al; N is nitrogen; each of R.sup.1 and R.sup.2 is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C.sub.1 C.sub.8 alkyl, C.sub.1 C.sub.8 perfluoroalkyl, alkylsilyl; x is the oxidation state on metal M; and n is from 1 to 6. Preferably, R.sup.1 and R.sup.2 of the aminosilane and metalloamide source reagent compositions are methyl and/or ethyl.

Description Paragraph - DETX (60):

By utilizing a precursor composition including at least one aminosilane source reagent composition and at least one metalloamide source reagent composition to produce a metal silicate dielectric thin film on a substrate, with the metalloamide source reagent composition containing at least part of the metal to be incorporated in the product dielectric metal silicate film, and the aminosilane source reagent compound containing at least part of the silicon to be incorporated in the product dielectric metal silicate film, it is possible by selection of the proportions of such respective compounds to correspondingly vary the stoichiometric composition (metal/silicon ratio) of the metal silicate dielectric film, to obtain a desired character of structural and performance properties in the product film. The relative proportions of the at least one aminosilane source reagent composition and the metalloamide source reagent composition relative to one another are employed to controllably establish the desired M.sub.x/Si.sub.1-x ratio in the deposited silicate thin films, wherein M.sub.x/Si.sub.1-x is from about 0.01 to 10. The exact composition will be a trade off between high Si films, which prevent crystallization during subsequent high temperature processing, and high M films, which have higher dielectric constant (lower EOT).

Description Paragraph - DETX (62):

In a further embodiment, the present invention relates to stable solutions for chemical vapor deposition (CVD) of silicon-containing thin films of varying types, including silicon nitride, silicon dioxide and doped silicon dioxide films (when a dopant co-precursor is utilized), wherein the stable solution comprises at least one aminosilane source reagent composition and at least one solvent component, in which the aminosilane source reagent composition is soluble or suspendable. Accordingly, the aminosilane source reagent composition and the at least one solvent component are combined to produce a precursor solution mixture for depositing a silicon containing thin film on the substrate.

Description Paragraph - DETX (68):

(1) vaporizing a precursor composition comprising at least one aminosilane source reagent composition made by reacting an aminosilane precursor compound with an amine source reagent compound in a solvent medium comprising at least one activating solvent component, to yield an aminosilane source reagent composition having a halogen content that is less than 1000 ppm, wherein said aminosilane source reagent composition is selected from the group consisting of: R.sup.3.sub.xSiA.sub.y(NR.sup.1R.sup.2).sub.4-x-y and (2)

Description Paragraph - DETX (69):

##STR00009## wherein R.sup.3 is selected from the group consisting of hydrogen, C.sub.1 C.sub.4 alkyl, and C.sub.1 C.sub.4 alkoxy; x is from 0 to 3; Si is silicon; A is halogen; Y is from 0 to 3; N is nitrogen; each of R.sup.1 and R.sup.2 is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C.sub.1 C.sub.8 alkyl, and C.sub.1 C.sub.8 perfluoroalkyl; and n is from 1 to 6;

Description Paragraph - DETX (71):

contacting the precursor vapor with a substrate in such chemical vapor deposition zone, at elevated temperature to deposit a corresponding silicon containing thin film.

Description Paragraph - DETX (72):

A wide variety of CVD process conditions may be utilized for chemical vapor deposition employing the compositions of the present invention. Typical liquid delivery MOCVD process conditions may include substrate temperature ranges of 160 to 300.degree. C., with about 170.degree. C. to about 250.degree. C. being more typical; vaporizer temperature ranges may be from about 50.degree. C. to about 150.degree. C., with about 60.degree. C. to about 100.degree. C. being

more typical; pressure ranges are generally from about 0.05 to about 20 Torr (and most preferably from about 0.1 to about 5 Torr), with a range of about 0.2 to about 0.5 Torr being more typical; and inert gas flows of helium or argon of from about 25 to 750 sccm (and most preferably from about 50 to about 200 sccm), at a temperature approximately the same as the vaporizer. In some cases, a co-reactant may be introduced (i.e., water, alcohol or hydrogen forming gas) to facilitate the film growth process.

Description Paragraph - DETX (74):

In one embodiment the aminosilane source reagent compositions of the instant invention may be used in an atomic layer chemical vapor deposition method, wherein the aminosilane source reagent composition is vaporized and introduced into a chemical vapor deposition chamber comprising a substrate, in a sequential or "pulsed" deposition mode, during which time, extremely co-reactive gases may be employed, such as ozone, water vapor or reactive alcohols, that might normally be expected to produce deleterious deposition effects on the CVD process (i.e., gas phase particle formation).

Description Paragraph - DETX (76):

In a further embodiment, a co-reactant may be used in a pulsed or atomic layer chemical vapor deposition method, wherein the metalloamide precursor and/or aminosilane precursor vapor is separated from the co-reactant by time in the pulse track. The co-reactant may be utilized to facilitate the decomposition of the precursor on a substrate, within a desired temperature regime and to produce carbon-free dielectric thin-films. As an example, the use of water vapor may be utilized to induce a lower decomposition temperature of the aminosilane precursor vapor, which in some instances has been found to be stable in oxidizing environments such as N₂O.

Description Paragraph - DETX (87):

In liquid delivery CVD, the source liquid may comprise the source reagent compound(s) if the compound or complex is in the liquid phase at ambient temperature (e.g., room temperature, 25.degree. C.) or other supply temperature from which the source reagent is rapidly heated and vaporized to form precursor vapor for the CVD process. Alternatively, if the source reagent compound or complex is a solid at ambient or the supply temperature, such compound or complex can be dissolved or suspended in a compatible solvent medium therefore to provide a liquid phase composition that can be submitted to the rapid heating and vaporization to form precursor vapor for the CVD process. The precursor vapor resulting from the vaporization then is transported, optionally in combination with a carrier gas (e.g., He, Ar, H₂, O₂, etc.), to the chemical vapor deposition reactor where the vapor is contacted

with a substrate at elevated temperature to deposit material from the vapor phase onto the substrate or semiconductor device precursor structure positioned in the CVD reactor.

Description Paragraph - DETX (88):

The precursor liquid may be vaporized in any suitable manner and with any suitable vaporization means to form corresponding precursor vapor for contacting with the elevated temperature substrate on which the dielectric film is to be formed. The vaporization may for example be carried out with a liquid delivery vaporizer unit of a type as commercially available from Advanced Technology Materials, Inc. (Danbury, Conn.) under the trademark SPARTA and VAPORSOURCE II, in which precursor liquid is discharged onto a heated vaporization element, such as a porous sintered metal surface, and flash vaporized. The vaporizer may be arranged to receive a carrier gas such as argon, helium, etc. and an oxygen-containing gas may be introduced as necessary to form the dielectric thin film. The precursor vapor thus is flowed to the chemical vapor deposition chamber and contacted with the substrate on which the dielectric film is to be deposited. The substrate is maintained at a suitable elevated temperature during the deposition operation by heating means such as a radiant heating assembly, a susceptor containing a resistance heating element, microwave heat generator, etc. Appropriate process conditions of temperature, pressure, flow rates and concentration (partial pressures) of metal and silicon components are maintained for sufficient time to form the dielectric film at the desired film thickness, (i.e., in a range of from about 2 nanometers to about 1000 micrometers), and with appropriate dielectric film characteristics.

Description Paragraph - DETX (89):

The step of vaporizing the source reagent compounds of the present invention is preferably carried out at a vaporization temperature in the range of from about 50.degree. C. to about 300.degree. C. Within this narrow range of vaporization temperature, the metalloamide and aminosilane source reagent compounds are effectively vaporized with a minimum extent of premature decomposition.

Description Paragraph - DETX (92):

The deposition of the silicon containing thin films of the present invention are preferably carried out under an elevated deposition temperature in a range of from about 250.degree. C. to about 750.degree. C.

Description Paragraph - DETX (97):

Silica films were grown with the silicon precursors listed in Table I, Si(NMe.sub.2).sub.3Cl and Si(NEt.sub.2).sub.2Cl.sub.2. Precursor solutions

were prepared at 0.1M Si in octane. Substrates of (100) Si were prepared with an SC1 treatment followed by dilute HF to remove any native SiO₂. The generic process conditions for the experiments are shown in Table II. Results from the growth of hafnia films encouraged the inventors to center initial experiments on growth in an N₂O atmosphere although growth in O₂ or other oxidizer could be used at temperatures at or below 500.degree. C. A limited pressure-temperature matrix was performed for each Si precursor using the N₂O ambient as shown in FIGS. 2A and 2B.

Description Paragraph - DETX (99):

TABLE-US-00002 TABLE II Generic process conditions Precursor solution 0.10M in octane Precursor solution delivery rate 0.10 ml/min Vaporization Temperature 150.degree. C. Run time 10 minutes Carrier gas 100 sccm Ar Heating and Cooling process gas 500 sccm Ar Run time process gas 400 sccm N₂O Pressure 0.8, 2.2, or 8.0 Torr Temperature 400 650.degree. C. wafer surface

Description Paragraph - DETX (105):

The films have a mixed Si:Hf composition on the film surface. The constant SiO₂ growth rate over the range of 500 600.degree. C. at 2.2 Torr being the same as 0.8 Torr at 600.degree. C. is taken as evidence of mass transport limited deposition over the range of the process. The addition of water vapor or O₂, should further decrease the temperature window wherein both Hf and Si alkylamido precursors transport and decompose reliably.

Description Paragraph - DETX (111):

The general reactions were carried out under a steady flow of nitrogen. A 5 L Schlenk flask was charged with 0.8 L of 1.6M solution of n-BuLi in hexane, 1 L of anhydrous hexane and a big magnetic stirring bar. Then 60 g (10% excess) of HNMe₂ was bubbled into the Schlenk flask slowly at 0.degree. C., under magnetic stirring. During the addition, very fine white precipitate of LiNMe₂ was formed and the reaction mixture became extremely viscous. The mixture was allowed to reach room temperature and then was stirred for an additional 2 h. A solution of SiCl₄ (43.5 g, 29.3 mL) in hexane (50 mL) was slowly added to the reaction flask. Moderate heat was generated (exothermic) and the external cooling to 0.degree. C. was applied. Upon completion of SiCl₄ addition, the mixture became less viscous. The mixture was allowed to reach room temperature and then was stirred for an additional 2 h. All volatiles were removed in vacuum. Then the reaction flask was charge with 0.5 L of anhydrous THF. The resulting mixture was refluxed for 4 h. THF was removed in vacuum to give a slurry-like mixture of Si(NMe₂)₄ and Li salts. 400 mL of hexane were added to extract Si(NMe₂)₄ and the resulting mixture was filtered. A second

extraction was applied with 100 mL of hexane and a slightly yellow filtrate was obtained. Removal of volatiles under vacuum followed by the vacuum distillation (35.degree. C. at 1 mmHg) gave 31.3 grams of colorless liquid. Yield: 60%. Bp. 35.degree. C. at 1 mmHg. Anal. (calcd., %): C 47.16 (47.06), H 11.42 (11.76), N 26.73 (27.45). Mass spectrum (EI, %): m/z 204 (M.sup.+, 70), 160 (M.sup.+ - NMe.sub.2, 100), 116 (M.sup.+ - 2 NMe.sub.2, 90). FIG. 7 .sup.1H NMR (C.sub.6D.sub.6): 2.51 (s, CH.sub.3). Residual Cl content is less than 10 ppm (detection limit of analysis).

Description Paragraph - DETX (113):

A 5 L Schlenk flask was charged with 0.8 L of 1.6M solution of n-BuLi in hexane, 1 L of anhydrous hexane and a big magnetic stirring bar. The reaction mixture was maintained at 0.degree. C. during the addition of HNEtMe (79.3 g, 1.344 mol, 5% excess) solution in hexane (100 mL). Very fine white precipitate of LiNEtMe formed immediately and the reaction mixture became extremely viscous. The mixture was allowed to reach room temperature and then was stirred for an additional hour. A solution of HSiCl.sub.3 (43.36 g, 0.32 mol) in hexane (100 mL) was slowly added to the reaction flask. Moderate heat was generated (exothermic) and the external cooling to 0.degree. C. was applied. Upon completion of HSiCl.sub.3 addition, the mixture became less viscous. The mixture was allowed to reach room temperature and then was stirred for an additional hour. All volatiles were removed in vacuum. Then the reaction flask was charge with 0.5 L of anhydrous THF. The resulting mixture was refluxed for 4 h. THF was removed in vacuum. 300 mL of hexane were added to extract amidosilanes, the resulting mixture was filtered, and the precipitate was discarded. Removal of volatiles under vacuum followed by the vacuum distillation gave two fractions (28.degree. C. at 0.5 mmHg and 50.degree. C. at 0.3 mmHg) in 4:3 molar ratios. The first fraction was confirmed to be HSi(NEtMe).sub.3. The second fraction was identified as Si(NEtMe).sub.4. Yield: 30%. Bp. 50.degree. C. at 0.3 mmHg. Anal. (calcd., %): C 55.61 (55.38), H 12.58 (12.31), N 21.08 (21.54). Mass spectrum (EI, %): m/z 260 (M.sup.+, 40), 202 (M.sup.+ - NEtMe, 70), 144 (M.sup.+ - 2 NEtMe, 50), 86 (M.sup.+ - 3 NEtMe, 100). .sup.1H NMR (C.sub.6D.sub.6): .quadrature.2.83 (8H, q, J(H--H)=7 Hz, CH.sub.2CH.sub.3), 2.51 (12H, s, CH.sub.3), 1.07 (12H, t, J(H--H)=7 Hz, CH.sub.2CH.sub.3). .sup.13C NMR: (C.sub.6D.sub.6) .quadrature.44.68 (CH.sub.2 CH.sub.3), 35.07 (CH.sub.3), 15.01 (CH.sub.2 H.sub.3).

Claims Text - CLTX (1):

1. A method of synthesizing an aminosilane source reagent composition, comprising: (a) reacting an aminosilane precursor compound with an amine source reagent compound, wherein the amine source reagent compound is selected from

the group consisting of: B(NR.^{sup.1}R.^{sup.2}) and ##STR00010## wherein B is selected from the group consisting of H, Li, Na, K, Zn and MgBr; N is nitrogen; R.^{sup.1} and R.^{sup.2} are same or different and each is independently selected from the group consisting of H, aryl, perfluoroaryl, C._{sub.1} C._{sub.8} alkyl, and C._{sub.1} C._{sub.8} perfluoroalkyl; and n is from 1 to 6, in a solvent system comprising at least one non-polar solvent, at temperature in a range from about -30.degree. C. to about room temperature, for a period of time sufficient to produce a reaction mixture comprising partially substituted aminosilane components, unreacted aminosilane precursors and unreacted amine components; (b) combining the reaction mixture with at least one polar activating solvent component to at least partially solvate and activate the unreacted amine components, wherein the polar activating solvent comprises a Lewis base selected from the group consisting of ethers and tertiary amines; and (c) continuing the reaction of step (b) at temperature in a range from about 0.degree. C. to about 100.degree. C. for a period of time sufficient to produce the aminosilane source reagent composition, wherein the aminosilane source reagent composition comprises less than 1000 ppm halogen.

Claims Text - CLTX (3):

3. The method according to claim 2, wherein the reactive leaving group is selected from the group consisting of H and halogen.

Claims Text - CLTX (5):

5. The method according to claim 1, wherein the aminosilane precursor compound is a silicon halide compound comprising a composition selected from the group consisting of: R.^{sup.3}.sub.xSiA._{sub.y}(NR.^{sup.1}R.^{sup.2}).sub.4-x-y and ##STR00011## wherein R.^{sup.3} is selected from the group consisting of hydrogen, C._{sub.1} C._{sub.4} alkyl, and C._{sub.1} C._{sub.4} alkoxy; x is from 0 to 3; Si is silicon; A is halogen; y is from 1 to 4; N is nitrogen; each of R.^{sup.1} and R.^{sup.2} is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C._{sub.1} C._{sub.8} alkyl, and C._{sub.1} C._{sub.8} perfluoroalkyl; and n is from 1 to 6.

Claims Text - CLTX (8):

8. A method of synthesizing an aminosilane source reagent composition, comprising the steps of: (1) combining an aminosilane precursor compound comprising at least one halogen leaving group, with an amine source reagent compound, in a solvent system comprising at least one non-polar solvent, for a period of time sufficient to produce a reaction mixture consisting essentially of partially substituted aminosilane components, unreacted aminosilane precursors and unreacted amine components; (2) combining with the reaction mixture of step (1) a polar activating solvent to at least partially solvate

and activate the unreacted amine components, wherein the polar activating solvent comprises a Lewis base selected from the group consisting of ethers and tertiary amines; (3) continuing the reaction of step (2) for a period of time sufficient to provide for essentially stoichiometric substitution of at least one halide on the aminosilane precursor compound by an amine component to produce the aminosilane source reagent composition.

Claims Text - CLTX (9):

9. The method according to claim 8, wherein the aminosilane source reagent composition comprises less than 1000 ppm halogen.

Claims Text - CLTX (11):

11. The method according to claim 10, wherein the reactive leaving group is selected from the group consisting of H and halogen.

Claims Text - CLTX (13):

13. The method according to claim 8, wherein the aminosilane precursor compound is a silicon halide compound comprising a composition selected from the group consisting of: $R_{3-x}SiA_y(NR_{1-x-y})_{4-x-y}$ and ##STR00012## wherein R_3 is selected from the group consisting of hydrogen, C_{1-4} alkyl, and C_{1-4} alkoxy; x is from 0 to 3; Si is silicon; A is halogen; y is from 1 to 4; N is nitrogen; each of R_1 and R_2 is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C_{1-8} alkyl, and C_{1-8} perfluoroalkyl; and n is from 1 to 6.

Claims Text - CLTX (18):

18. The method according to claim 8, wherein the reaction of steps (2) and (3) is carried out at a temperature that is in the range of from about -30.degree. C. to room temperature.

Claims Text - CLTX (19):

19. The method according to claim 8, wherein the reaction of steps (2) and (3) is carried out at a temperature that is in the range of from about 0.degree. C. to 100.degree. C.

Claims Text - CLTX (23):

23. The method according to claim 8, wherein the amine source reagent compound comprises an amine having a composition selected from the group consisting of $B(NR_{1-x-y})_{4-x-y}$ and ##STR00013## wherein B is selected from the group consisting of H, Li, Na, K, Zn and MgBr; N is nitrogen; R_1 and R_2 are same or different and each is independently selected from the group

consisting of H, aryl, perfluoroaryl, C.sub.1 C.sub.8 alkyl, and C.sub.1 C.sub.8 perfluoroalkyl; and n is from 1 to 6.

Claims Text - CLTX (25):

25. A method of synthesizing an aminosilane source reagent composition, comprising the steps of: (1) combining an aminosilane precursor compound comprising at least one halogen leaving group, with an amine source reagent compound, in a solvent system comprising at least one non-polar solvent, for a period of time sufficient to produce a reaction mixture consisting essentially of partially substituted aminosilane components, unreacted aminosilane precursors and unreacted amine components; (2) removing the non-polar solvent from the reaction mixture; (3) combining with the reaction mixture of step (2) a polar activating solvent to at least partially solvate and activate the unreacted amine components; (4) continuing the reaction of step (3) for a period of time sufficient to provide for essentially stoichiometric substitution of at least one halide on the aminosilane precursor compound by an amine component to produce the aminosilane source reagent composition.

Current US Cross Reference Classification - CCXR
(3):

438/790

Other Reference Publication - OREF (10):

Kozoh Sugiyama, et al., "Low Temperature Deposition of Metal Nitrides by Thermal Decomposition of Organometallic Compounds", Journal of the Electrochemical Society, vol. 122, No. 11, Nov. 1975. cited by other

Other Reference Publication - OREF (12):

Toshiro Maruyama, et al., "Silicon dioxide thin films prepared by chemical vapor deposition from tetrakis(diethylamino)silane and ozone", Applied Phys. Lett. 64, (21), May 23, 1994. cited by other

Other Reference Publication - OREF (13):

Toshiro Maruyama "Electrical Characterization of Silicon Dioxide Thin Films Prepared by Chemical Vapor Deposition from Tetrakis(diethylamino)silane and Ozone", Jpn. J. Appl. Phys. vol. 36 (1997) pp. L922-925, Part 2, No. 7B, Jul. 15, 1997. cited by other

Other Reference Publication - OREF (14):

Chi Ming Yam, et al., "Simple Acid-Based Hydrolytic Chemistry Approach to Molecular Self-Assembly: Thin Films of Long Chain Alcohols Terminated with Alkyl, Phenyl, and Acetylene Groups on Inorganic Oxides Surfaces", Langmuir,

(1998), vol. 14, No. 24, pp. 6941-6947. cited by other